CHAPTER 1

LITERATURE REVIEW

Introduction

The fate of a herbicide applied to soil is governed to a large extent by its adsorption on soil colloids, desorption of the adsorbed fraction, its degradation and persistence (Briggs, 1984; Rahman, Krishna & Rao, 1988). Herbicides dissipate from soil by a variety of means. Some of the more important avenues of dissipation are chemical degradation, leaching, microbial degradation, uptake by plants, photodecomposition and volatilization (Bailey & White, 1970; Weber, 1970a,b; Goring & Hamaker, 1971; Swann & Eschenroeder, 1983; Weber, 1991a). Weber (1991a) presented a review on the many chemical, physical and biological processes involved in the dissipation of herbicides in the environment. By definition, dissipation infers that "the herbicide is transformed into by-products, which are further transformed, and that the parent herbicide and its by-products are also transferred to other places and transformed until none exists, or in most cases none is detectable". Hence the many processes in the dissipation of herbicides are categorized as transfer processes or transformation processes (Dubach, 1970; Weber, 1991a).

Transfer processes are characterized by the chemical molecule remaining unchanged. Transfer mechanisms include adsorption to and desorption from soil colloids, absorption, exudation and retention by plants, movement on the soil surface, volatilization, and leaching or capillary movement. The transformation processes cause

loss of integrity of the chemical molecule. These processes include degradation by chemical, photochemical or biological means. Transformation of a chemical can occur during any of the transfer modes.

There is considerable interest in atrazine and other *s*-triazine herbicides because of their extensive use in agriculture, their persistence in soil, effects on succeeding crops, and movement into surface and groundwater. The herbicidal activity, mode of action, and fate of atrazine in biological and soil systems have been extensively reviewed by Esser, Dupuis, Ebert, Marco & Vogel (1975). Erickson & Lee (1989) reviewed factors involved in the degradation of atrazine and related *s*-triazines. Nel & Reinhardt (1984) reviewed factors which affect the activity of atrazine in plants and soil, and also reported on research conducted locally. The present treatise on the documented fate of atrazine in the environment will be concerned primarily with the dissipation of the herbicide in soil. Comprehensive reviews on the effects of soil factors on herbicide activity have been presented by Riley & Morrod (1976), Eagle (1976), Walker (1980), Hance (1983) and Weber (1991a). Similar effects of soil would be expected for herbicides with comparable chemo-physical characteristics, because the movement and uptake of herbicides in soil depend on the soil/chemical interaction; and not on herbicide bioactivity which is only expressed when the chemical reaches the active site in the plant. Hence the literature citations in the present review include those studies in which atrazine featured, and situations in which other compounds behaved in a manner similar to atrazine.

TRANSFER PROCESSES

Adsorption on soil colloids

Herbicide adsorption is dependent on soil chemical and physical properties, structure of the herbicide and environmental factors such as temperature and soil water content. Schiavon (1988) and Hubbs & Lavy (1990) found that adsorption determines movement of the herbicide in soil, including leaching to groundwater. Adsorption also reduces the availability of atrazine for absorption by plants, thereby reducing herbicide bioactivity (Dao & Lavy, 1978).

The availability of atrazine for absorption by plant roots is dependent on the adsorption-desorption equilibrium being shifted towards the desorption side. This equilibrium must be expected to be quite variable due to the involvement of the different, often interrelated, constituents of the solid soil phase. These soil constituents include clays, hydrous oxides of iron and aluminium, organic material and various other organic substances (Dubach, 1970; Hayes, 1970; Weber, 1970a,b; Weber, 1991a). Green & Obien (1969) and Dubach (1970) contend that the dynamic and open nature of soil, absorption by plants and microorganisms, and degradation processes ensure that equilibrium with respect to herbicide concentration between the adsorbed and solution phases is never reached.

It has been shown that herbicides generally, and the triazines particularly, are reversibly adsorbed on the organic matter and clay mineral fractions in soils (Frissel, 1961; Talbert & Fletchall, 1965; Weber, 1970a,b; Hayes, 1970; Schiavon, 1988). Several

studies revealed that soil organic matter is the most important soil factor as far as atrazine adsorption or bioactivity is concerned (Talbert & Fletchall, 1965; Weber, Weed & Ward, 1969; Harrison, Weber & Baird, 1976; Rahman & Matthews, 1979; Anderson, Stephenson & Corke, 1980). In spite of relatively low organic matter contents in South African soils, Smit, Nel & Fölscher (1980), Nel & Reinhardt (1984) and Ehlers, Reinhardt & Nel (1987, 1988) found that the organic carbon content (% C) of soil was strongly and negatively correlated with atrazine bioactivity. In all the above-mentioned studies, organic matter content consistently predicted atrazine availability better than either cation exchange capacity (CEC), total clay content or individual clay minerals. According to Eagle (1983b), a positive relationship usually exists between the clay and organic matter content of soils, but problems tend to occur when this is not the case, and the recommendations for herbicide rates to be applied are based solely on the clay content of soils. In these situations, either excessive bioactivity, which may lead to crop damage, or low bioactivity resulting in poor weed control may be expected.

Weber (1991a) states that organic matter, clay minerals and sesquioxides represent the active fraction of soil, and silt and sand the inactive fraction. The active fraction, which is involved in chemical reactions in the soil, is colloidal in nature, i.e. the constituents representing this fraction are organic and inorganic substances with a small particle size (< 0.001 mm) and a resulting large surface area per unit mass. According to Weber (1991a), it can be expected that the tilled surface soil is a relatively homogeneous mixture of the active and inactive fractions. Weber (1991a) reviews the important characteristics of soil colloids which pertain to their ability to adsorb

herbicides. Properties of soil colloids involved in adsorption of herbicides are briefly discussed here.

Weber (1991a) contends that organic matter is more flexible than clays with respect to the ability to adsorb a wide assortment of herbicides. Some degree of solubility is required of herbicides to become retained at the highly hydrated hydrophilic surfaces of clay particles, whereas organic matter has both hydrophilic and lipophilic characteristics which enables it to react with herbicides of wide ranging solubility and ionizability. According to Kononova (1966), and Weber, Swain, Strek & Sartori (1986), humified substances (humus) make up 17 to 97% of the total organic carbon in a soil. Humus consists predominantly of humic acids which are high molecular mass compounds with functional groups and aromatic rings which are lipophylic in nature and which possess numerous ionizable carboxyl and hydroxyl groups that give the polymer pH dependent exchange properties (Kononova, 1966).

Bohn, McNeal & O'Connor (1985) list some important characteristics of certain clay minerals which adsorb herbicides. The two major types of clay minerals present in soils are the 1:1 and 2:1 (silica:alumina) types (Brady, 1974). Kaolinite (1:1 clay mineral) does not exhibit high-intensity colloidal properties because of its limited adsorptive capacity for cations and a relatively low surface area. The intensive study of Frissel (1961) focused on the important role of montmorillonite and to a lesser extent illite and kaolinite in the adsorption of triazines in soil. Talbert & Fletchall (1965) reported that kaolinite at pH 5 and pH 7 did not adsorb either atrazine or simazine. In the 2:1 expanding type of clay, montmorillonite, there is a very large internal surface

which far exceeds its external surface area. The combined internal and external surfaces (specific surface area) of montmorillonite greatly exceeds the surface area of kaolinite.

The oxides and hydrous oxides of iron and aluminium are intermixed with silicate clays in temperate regions. They are prominent in tropical and sub-tropical soils in several mineralogical forms, including boehmite, gibbsite, goethite and hematite (Brady, 1974; Brown, Newman, Rayner & Weir, 1978). These minerals have a pH dependent charge, and therefore may exist as positive, neutral, or negatively charged particles. The hydrous oxides have a much smaller CEC than kaolinite. In South Africa the amorphous Fe-Al-OH component is commonly found in acid soils in which kaolinite predominates. The Fe subfraction tends to be bonded strongly to crystalline minerals such as kaolinite, whilst the more weakly bonded Al fraction carry active positive charge (Fouché & Brandt, 1973). Smit, Nel & Fölscher (1980) suggested that atrazine can be bonded to the positive charge of Al of the (Fe.Al.OH) component through free electrons on the N atoms of amine groups and/or N atoms in the ring structure of atrazine. In the light of increased atrazine bioactivity that was caused by increases in the pH and the phosphorus level in soil, they construed that increases in OH^- and $H_2PO_4^-$ neutralised the adsorptive capacity of the amorphous component for atrazine.

There are two general sources of CEC for inorganic colloids: (a) permanent negative charge that results from isomorphic substitution, and (b) pH dependent charge which results from the ionization of hydrogens from hydroxyl (OH) groups located at the edges of micelles and from iron and aluminium hydroxides (Anderson, 1983). The

greater surface area of the expanding type clays, combined with a much greater CEC, endows them with a much greater propensity for binding herbicides than the non-expanding types (Weber, 1972; Weber, Shea & Weed, 1986).

Adsorption theories and equations

Atrazine has a low vapour pressure (0.08 mPa at 25°C), which makes adsorption at the solid-water interface, and not adsorption at the solid-gas interface, the dominant phenomenon in soil treated with this herbicide (Calvet, 1980). The herbicide exists in the soil in two phases: solution and sorbed. The total amount of herbicide, solution plus sorbed fractions, decreases with time due to degradation, but at any time follows the mass conservation equation: $m = Vc + Mx$. In this equation, m is the total mass (μg) of the herbicide in the system, V is the volume of water (ml) in the system, c is the herbicide concentration (μg ml^{-1}) in water phase, M is the mass (g) of soil in the system, and x is the herbicide concentration (μg^{-1}) in the sorbed phase. According to Calvet (1980), knowledge of solute concentrations only is deemed sufficient for the adsorption process to be described, usually as an adsorption isotherm, i.e. the relationship between amount adsorbed and solution concentration. Isotherms that describe herbicide adsorption in aqueous solutions (soil-water systems) have been derived empirically. Weber (1991a) states that the relatively low solubility of most herbicides, and the lack of knowledge about adsorption mechanisms also limit the value of equations to describe adsorption.

The effect of adsorption on herbicide availability in the soil solution can be estimated from adsorption coefficients which are derived from adsorption theories. The empirical

Freundlich equation (1) can be rearranged to obtain a distribution coefficient (K_d) for a given herbicide in a given soil as shown in Equation 2 (Weber, 1991a).

$$X = KC^{n^{-1}}$$

X = quantity of herbicide (nmol) adsorbed to a mass (1 g) of soil

C = concentration of herbicide in solution (nmol ml^{-1})

K = constant which reflects adsorption capacity

n^{-1} = constant which reflect intensity of binding

$$K_d = \frac{X}{C^{n^{-1}}}$$

K_d = distribution coefficient

Riley (1978) found that the K_d value for atrazine varies between about 1 and 3, the latter value being typical in loam soil containing 3% organic matter. Herbicides with a $K_d < 10$ are classified as mobile in soil (Riley, 1991).

K_d values are normally highly correlated with the organic matter contents of soils, increasing as organic matter content increases (Weber, 1991a). Knowing the percentage of organic carbon of a soil, and assuming that herbicides are adsorbed only to organic surfaces (most applicable to nonionic, lipophilic herbicides), a K_{oc} value (partition coefficient) for a given herbicide adsorbed by a particular soil may be calculated using Equation 3 (Weber, 1991a).

$$K_{oc} = \frac{K_d}{\%OC} \times 100 \qquad\qquad _____3$$

K_{oc} = partition coefficient

oc = organic carbon content of soil (%)

K_{oc} values calculated for selected herbicides, as well as certain other key properties appear in Table 1.

An assumption associated with the Freundlich equation is that the herbicide adsorption-desorption process is a reversible equilibrium that is attained during the time period of the experiment (Clay, Allmaras, Koskinen & Wyse, 1988). However, it has been reported *inter alia* by Calvet (1980) and Clay & Koskinen (1990) that desorption of organic chemicals from the soil is not satisfactorily predicted by the adsorption Freundlich equation. Difference in the adsorption and desorption isotherms is known as hysteresis. Non-extractable herbicide fractions are termed "fixed". Best & Weber (1974) found that this plant-unavailable fraction range from 4.6 to 23% for atrazine and prometryn, depending on the pH of the system. A literature review by Rahman *et al.* (1988) revealed that much less attention has been paid to desorption as compared to adsorption.

Table 1 Classification and key properties of atrazine and selected ionic herbicides (from Weber, 1991a; originally from Weber, 1972, 1987)

Category	Common name	Species	pKa	Water solubility ($mg\ L^{-1}$)	Vapour pressure (mPa)	Soil K_{OC}	Half-life (days)
Strong base	paraquat	$R\text{-}N^{+2}$	>9	1×10^6	<0.01	$10^5\text{-}10^6$	100-400
Phosphonic acid	glyphosate	PO_3^{-1}; PO_3^{-2}	3.7; 10	1.6×10^4	<0.001	$10^4\text{-}10^5$	20-40
Moderate base	prometryn	molecule; cation	4.1	52	0.27	300-600	30-60
Weak base	**atrazine**	molecule; cation	1.7	30	0.08	150-300	25-50
Very weak base	metribuzin	molecule; cation	1.0	1300	<0.13	20-60	15-30
Very weak acid	bromacil	molecule; anion	9.1	815	0.033	30-60	60-120
Strong acid	dalapon	molecule; anion	1.5	1×10^6	<0.13	1-2	3-10

Adsorption mechanisms

Details of the types of herbicide adsorption isotherms and mechanisms have been discussed by Weber & Miller (1989). Evidence that Van der Waals forces, ion exchange, hydrogen bonding and complexation are involved in the adsorption of triazines on organic matter is thoroughly reviewed by Hayes (1970). Bailey & White (1970) categorized mechanisms of adsorption of organic chemicals on clay minerals. Postulated mechanisms of adsorption between organic molecules and organic and mineral adsorbants are the following:

(i) Ionic bonds. This type of bonding involves chemical adsorption due to attraction of opposite unit charges between adsorbate and adsorbent (Anderson, 1983). Adsorption by ionic bonds is due to ion exchange, a process in which the N atoms in the atrazine molecule would be protonated, resulting in the molecule existing as a cation in the soil system. In general, chemical adsorption is of high bonding strength.

The findings of Kononova (1966) and Sullivan & Felbeck (1968) suggest that protonated atrazine molecules may be bonded to carboxyl anions (-COO⁻) on the colloidal surface, and that this adsorption mechanism is pH dependent. In moderately to strong acid soils the hydrogen is apparently tightly held by covalent bonding on the colloidal surface, and is therefore not subject to ready displacement by other cations. A negative colloidal surface charge is therefore not apparent under acid soil conditions (Brady, 1974), thus precluding extensive ionic binding of organic bases. Hayes (1970) is of the opinion that ion exchange can account only for a small fraction of adsorption on organic colloids, since humic acids ionize at pH values lower than those normally encountered in soil. The magnitude of the pH dependent colloidal charge varies with the type of colloid.

It is the dominant type of charge for organic colloids, and accounts for most of the charge of the 1:1 type clay minerals and up to one fourth of that of some 2:1 types (Brady, 1974).

(ii) <u>Coordinate bonding</u>. Coordination compounds (metal atom complexes) form when an atom or ion of a metal is surrounded and bonded by a cluster of ions or molecules. This cluster is referred to as a ligand. Such interactions are possible with the water molecule usually being the exchange ligand. Weber *et al.* (1969) contend that atrazine may be adsorbed by complex formation. However, according to Hance (1971), it is unlikely that atrazine is adsorbed in this way.

(iii) <u>Hydrogen bonds</u>. Hydrogen bonding occurs when a hydrogen atom is attracted to two highly electronegative atoms (Anderson, 1983). Hydrogen bonds of appreciable strength only occur in molecules containing highly electronegative atoms, such as oxygen, nitrogen, bromine, sulphur, carbon and chlorine; so that all herbicides are involved. In spite of the limitation of not very convincing experimental proof (Calvet, 1980), two kinds of hydrogen bonds have been described: (a) between adsorbed water molecules and adsorbed organic molecules; (b) between surface groups (e.g. oxygen atoms) and organic molecules. The first type has been suggested by Calvet & Terce (1975a) to be a mechanism for the adsorption on montmorillonite of atrazine. Hayes (1970) is of the opinion that adsorption by hydrogen bonds between the secondary amino groups of the atrazine molecule and the carbonyl group (-C=O) of organic material (carbonyls and ketones) is more important than is generally accepted.

(iv) <u>London-Van der Waals bonds</u>. These are due to physical forces (dispersion forces) which result from the interaction of the positive and negative charges between neighbouring atoms (Anderson, 1983). In general, physical adsorption is of low binding strength and probably exists with all herbicides (Calvet, 1980). Physical adsorption by Van der Waals forces is temperature-dependent. At high temperatures, the kinetic energy of the atrazine molecule is higher than the energy involved in Van der Waal bonds, thereby rendering this adsorption mechanism irrelevant according to Hayes (1970).

Weber (1991a) explains that the complexity of the soil system due to its many phases, including solids, colloids, soil solution, solutes, gases such as CO_2 and O_2 and vapours of herbicides and other organics, precludes adequate descriptions of adsorption-desorption reactions of herbicides in soils. The many different adsorption mechanisms that are possible, depending on the chemical and physical properties of the herbicides involved, further confound the issue. This aspect is illustrated by the grouping of atrazine and selected herbicides into seven categories (Weber, 1972; Weber, 1987) in Table 1 on the basis of key properties.

Influence of soil pH, water content, electrolyte concentration and temperature on adsorption

The primary roles of the physico-chemical properties of both the herbicide and the soil colloids in the adsorption-desorption phenomenon have been discussed above, but the availability of atrazine for absorption by plant roots is known to be directly or indirectly

influenced by several other factors. Although identification of the individual effects of soil factors involved in herbicide bio-availability is often complicated by interrelationships between them, several factors which affect atrazine adsorption have been documented.

Soil pH

According to Appleby (1985), soil pH has an important influence on the adsorption, and therefore, the availability of atrazine for uptake by plants. Soil pH influences triazine adsorption through its effect on both the chemical structure of the herbicides and soil adsorption sites. Weber & Whitacre (1982) found that atrazine is a weak base in aqueous solution and exists as a molecular species at high pH, and cations at low pH. Only atrazine in the cation form would be subject to adsorption on soil colloids with negative charge, thus explaining its increased adsorption and lower phytotoxicity at low pH in most soils. It was shown by Colbert, Volk & Appleby (1975) that adsorption of atrazine and terbutryn decreased on natural and limed soils as the soil pH increased to pH 8. Best & Weber (1974) found that the total amount of atrazine and prometryn applied was absorbed by plants over a five-month period ranged from 0.6 to 4.3% and was closely linked to the pH of the soil, with higher herbicide concentrations occurring in the plants at the higher soil pH level (7.7) compared to the lower pH (5.5). Consistent with the reported decrease in *s*-triazine adsorption with increased pH, Smit *et al.* (1979, 1980) showed that the phytotoxicity of atrazine in some soils was increased by increases in the soil pH from below pH 5 to about pH 6. They attributed this effect to increased availability of atrazine for uptake by plants, and also to increased stability of atrazine molecules at the higher pH levels.

Several studies revealed that adsorption of s-triazines increased with a concomitant decrease in soil pH (McGlamery & Slife, 1965; Talbert & Fletchall, 1965; Weber, 1970b; Yamane & Green, 1972; Marshall, Nel & Smit, 1982). Protonation of atrazine molecules, and subsequent adsorption at negatively charged sites on soil colloids, progressively increases as soil pH decreases. Weber (1970b) suggested that atrazine may be bonded by complexation with protons on clay surfaces under acid conditions. Maximum adsorption of atrazine may be expected to occur near the pKa value (1.68) for this herbicide (McGlamery & Slife, 1965; Weber, 1970b). Reduced sorption is possible at pH levels lower than the pKa value, because of increased competition between hydronium ions (H_3O^+) and atrazine (cations$^{(+)}$) for negatively charged sites on soil colloids.

Harris & Hurle (1979) showed that atrazine and simazine adsorption onto clay colloids are highly sensitive to minute changes of soil solution pH and that plants can play an important role here by bringing about such changes in pH through ion exchange. They theorized that since triazine adsorption is so highly sensitive to pH changes, any change in rhizosphere pH through ion exchange or microbial activity must affect the adsorbed/solution herbicide equilibrium and, therefore, the amount of herbicide immediately available to the plant.

Soil water

The availability of atrazine for uptake by underground plant parts is influenced directly by soil water content, since water is the medium in which atrazine is transported and from which it is adsorbed. Green & Obien (1969), Bailey & White (1970) and Appleby

(1985) found an inverse relationship between atrazine adsorption and soil water content. Dao & Lavy (1978) suggested that soil water depletion would increase the atrazine concentration in soil solution, allowing polar atrazine molecules to compete favourably with a reduced number of water molecules for binding sites on soil colloids. Green & Obien (1969) were of the opinion that atrazine mobility in soil, and not fluctuations in atrazine concentration in soil solution *per se*, governed herbicide availability at the root surface. Several studies indicated that atrazine phytotoxicity was linked to soil water content, with increases in bioactivity as soil water content increased (Lavy, 1968; Dao & Lavy, 1978; Nel & Reinhardt, 1984).

According to Ammon (1985), leaching depth is a function of herbicide mobility, persistence, weather factors and percolating water. These parameters need to be considered in estimations of the potential of a herbicide to contaminate underground water. Leaching of a herbicide beyond the root zone is dependent on the amount, frequency and intensity of water received. Apart from temperature, which has a significant effect on microbial activity and hence the persistence of compounds, the most important climatic characteristics relating to pesticide leaching are the duration of the "field capacity period" and the amount of "excess rain" during this period (Hollis, 1991). According to Talbert & Fletchall (1965) and Nel (1975), most of the atrazine applied at normal rates can be leached out of the root zone, but those fractions adsorbed on the internal surfaces of 2:1 swelling type clays, such as montmorillonite, would be least subject to leaching. Based on K_{oc} values, atrazine (K_{oc} = 102 to 163) is classified as moderately to slightly mobile (Leonard *et al.*, 1988). Because of the pH dependent adsorption of atrazine on soil colloids, the herbicide is more susceptible to leaching

under neutral and alkaline than under acid conditions (McGlamery & Slife, 1965; Smit & Nel, 1977).

Coarse-textured soils, which are low in organic matter and clay, would be particularly susceptible to atrazine leaching because these soils have limited sorption capacity. Fleming, Wax & Simmons (1992) contend that continued registration of atrazine for use in these soils may depend on development of formulation or application methods that reduce leaching potential. Controlled release formulations may have promise for reducing the mobility of atrazine. Fleming *et al.* (1992) showed that a starch-encapsulated atrazine formulation (granules 20-40 mesh) should result in relatively fast atrazine release (compared to release from large granules of 14-20 mesh) and improved weed control (compared to weed control provided by the large granules and a commercial dry flowable formulation), while still reducing the leaching potential of atrazine.

According to Spencer & Cliath (1973), herbicides in the unsaturated soil solution may undergo some net upward movement with water as it moves from high to low potential via evaporation from the soil surface. Hubbs & Lavy (1990) states that the magnitude of this effect is proportional to the adsorbed and soil solution amounts of a compound. These researchers found that evaporation of water from the soil surface, and consequent upward movement of atrazine with capillary water, may be important in the dissipation of the herbicide. They also reported significant atrazine losses from plain glass slides and ascribed them to volatilization. However, a soil coating on the glass slides reduced ^{14}C volatility losses for atrazine from 81 to 7%. Although these laboratory studies

suggest that capillary movement is important to the volatilization loss of atrazine, it remains doubtful that volatilization is an important avenue of dissipation of atrazine under field conditions.

Water solubility is often regarded as an indicator of adsorption and leaching. Retention of urea and triazine herbicides in the upper layers of the soil profile was originally attributed to their low water solubility. As discussed by Hartley (1976), it was subsequently recognized that adsorption by soil, not insolubility, was the most important factor retarding the movement of chemicals through soil. According to Briggs (1984), there is an inverse relationship between solubility and K_{ow} and hence K_d for liquids, whilst for solids an additional factor is the energy required to disrupt the crystal structure. This is related to the melting point (T_m) of the chemical (Briggs, 1981a) by the equation:

$$\text{log water solubility (mole ml}^{-1}) = -\log K_{ow} - 0.01(T_m - 25) \quad \text{\_\_\_\_\_4}$$

It can be calculated that there can be a 1000-fold variation in water solubility between a liquid and a high melting point solid of the same K_{ow} and a corresponding 36-fold difference in K_d for compounds of the same water solubility (Briggs, 1984). Nicholls, Briggs & Evans (1984) showed that there are few chemicals for which water solubility is an important feature of their behaviour in soil. After an initial equilibration period all soil-applied herbicides are either adsorbed or dissolved at normal field rates, water solubility being a factor only for simazine and lenacil, each with log K_{ow} < 2 and a high melting point (Briggs, 1984). The log K_{ow} values/melting points for atrazine and simazine are 2.0-2.5/173°C and 1.5-2.0/225°C, respectively. From equation (4), the

water solubility of atrazine (33 mg L^{-1} at 25°C) would be expected to be higher than that for simazine (3.5 mg L^{-1} at 20°C).

Weber (1991a) states that organic matter is more universal in its ability to react with a wide assortment of herbicides with varying degrees of solubility and ionizability. Grover (1965) contends that under high soil water conditions, the availability of atrazine will predominantly be determined by the extent of its adsorption on the hydrophobic adsorptive sites on organic colloids. Under high soil water conditions adsorption on hydrophilic sites could be insignificant because atrazine would be readily desorbed from these sites by the overwhelming number of highly polar water molecules. Under low soil water conditions the availability of hydrophilic adsorptive sites will affect the bioactivity of atrazine. As the water content in the soil is decreased, more atrazine will be adsorbed on the now accessible hydrophilic surfaces (Grover, 1965).

Electrolyte concentration in soil solution

The differential availability of nutrients and soil-applied herbicides for uptake by plants depends on differences in their solubility in the soil solution and the extent and strength of adsorption. Hurle & Freed (1972) found that atrazine and simazine adsorption increased in the presence of rather high electrolyte (NH_4^+, K^+, Ca^{++}) concentrations and ascribed this effect to depressed herbicide solubility. Since the replacing power of cations on clay and humus in general follows the order $C^+ < C^{++} < C^{+++}$ (Brady, 1974), the divalent Ca^{++} ions would cover more of the negative adsorption sites and were more strongly adsorbed than the monovalent K^+ and NH_4^+ ions (Hurle & Freed, 1972). Herbicide adsorption could, therefore, be limited by competition between

atrazine and cations for negatively charged adsorption sites, thereby increasing the concentration of atrazine in the soil solution. These findings were corroborated when Dao & Lavy (1978) showed that atrazine adsorption increased with an increase in the concentration of KCl and NH_4Cl in the soil solution. However, the electrolytic effect of $CaCl_2$ was comparatively low, probably because of competition between Ca^{++} and atrazine for adsorption sites (Dao & Lavy, 1978). Hurle & Freed (1972) are of the opinion that the effect of electrolyte concentration is negated under field conditions by constantly changing uptake by plants, dilution or precipitation.

Temperature

Temperature affects herbicide activity in various ways, often interrelated with other environmental factors. According to Appleby (1985), temperature affects the bioactivity of atrazine by influencing its adsorption in soil, absorption by plants, and fate in plants.

Several researchers have shown that increasing temperatures result in decreased adsorption of atrazine on clay colloids (McGlamery & Slife, 1965; Talbert & Fletchall, 1965). In contrast, McGlamery & Slife (1965) also found that adsorption of atrazine on a humic acid increased as temperature increased being nearly twice as great at 40°C than at 0.5°C. This is opposite of what usually occurs with mineral systems (Bailey & White, 1970). McGlamery & Slife (1965) concluded that the adsorption phenomena that occur on isolated humic acids may not be the same as those occurring with natural soil organic matter. There was very little desorption from the humic acid, but desorption of atrazine in a soil increased as temperature increased, desorption being

nearly complete at 30°C. According to McGlamery & Slife (1965), increases in temperature should increase desorption as desorption is endothermic.

Temperature is believed to exert an indirect influence on the adsorption process through its effect on herbicide solubility. Bailey & White (1970) reported the existence of an inverse relationship between the degree of adsorption and solubility within a number of herbicide groups, in particular *s*-triazines. McGlamery & Slife (1965) suggested that solubility play a role in the temperature effect on desorption as the solubility of atrazine is only 22 mg L^{-1} at 0°C, while it is 70 and 320 mg L^{-1} at 27 and 85°C, respectively.

Absorption and retention by plants

Plants respond to herbicides only after absorption and translocation of the compound to the site of action in plants. Lavy (1970) showed that uptake of *s*-triazines occurs primarily from free herbicide in soil water. Herbicides that enter the roots and are readily translocated to the site of action in the plant include amitrole, dalapon, *s*-triazines, TCA and ureas (Anderson, 1983). Soil-applied atrazine is absorbed mainly by the roots and translocated in the apoplast system along a water gradient established by water loss through transpiration (Ashton & Crafts, 1981). Minshall, Sample & Robinson (1977) linked increased uptake of atrazine by tomato (*Lycopersicon esculentum* Mill.) plants to increased flow of the xylem stream. They also found that the uptake mechanism tended to maintain a constant concentration of atrazine in the xylem stream of plants.

Robinson & Dunham (1982) were able to predict the uptake of atrazine and terbuthyl-azine by oats seedlings on the basis of the mass flow theory. It is conceivable that metabolism of atrazine to hydroxyatrazine in root tissue causes absorption of more atrazine because this conversion reduces the concentration of atrazine in the cells and more atrazine diffuses into the tissue down the concentration gradient (Price & Balke, 1983).

Norris & Fong (1983) suggested that differences in atrazine metabolism, in conjunction with the altered partitioning between polar and nonpolar plant components, could lead to differential herbicide uptake. Phillips, Egli & Thompson (1972) found that soybean (*Glycine max* Merr.) seeds absorbed atrazine in relatively large quantities, and explained it in terms of the compatibility of this nonpolar (lipophilic) herbicide with the oil in the seed.

The site of absorption for a single herbicide can differ among plant species. Atrazine is most effective when placed in the shoot zone of green foxtail (*Setaria viridis* L.), giant foxtail (*Setaria faberi* Herrm.) or radish (*Raphanus sativus* L.) (Knake, Appleby & Furtick, 1967; Knake & Wax, 1968; Shone & Wood, 1976), whereas it appears to enter wild oat (*Avena fatua* L.) plants primarily by root uptake (Nishimoto, Appleby & Furtick, 1969). Since herbicides are carried to the roots by mass flow (fast process) and to the underground shoots by diffusion (slow process), the effect of soil water on the phytotoxicity of atrazine may differ among plant species (Moyer, 1987).

Absorption and retention of herbicides by weeds and crop plants is also dependent on the characteristics of the chemical (Ashton & Crafts, 1981; Fedtke, 1982). Mobility in and out of plants is often correlated with herbicide solubility - mobility increasing as solubility increases (Weber, 1991a). According to Weber (1991a), the amount of a mobile herbicide normally absorbed and retained by plants can reach about 5% of the total amount applied. Best & Weber (1974) found that the total amount of atrazine absorbed and retained by plants over a five-month study ranged from 1.6 to 4.3% of the total amount applied; and was very dependent on the pH of the soil, higher herbicide concentrations occurring in the plants at pH 7.7 than at pH 5.5.

Hoffman & Lavy (1978) showed that plants grown in atrazine-treated soils compete for the plant-available atrazine fraction. In their bioassay studies, high plant populations were not as effective as low plant populations in detecting low levels of atrazine in soil. Conversely, by increasing plant populations or decreasing soil volumes, quantitative measurement of higher atrazine concentrations could be determined. According to Weber (1991a), high weed populations may result in much higher amounts of plant-mobile herbicide being removed from the soil, but amounts rarely exceed 10% of that applied, and that which is taken up by crop plants is normally inactivated. The amount of herbicide and metabolites removed by crop plants is normally less than 5 mg kg^{-1} and the amount deposited in crop seeds is generally non-detectable at levels lower than 1 pg kg^{-1} (Weber, 1991a).

Nelson & Khan (1992) demonstrated that hyphae of vesicular-arbuscular fungi (naturally occurring root symbionts found in many plant species) remove atrazine from soil and transfer the herbicide to maize plants.

Mechanism of action

Vostral, Buchholtz & Kust (1970) suggested that differences in the resistance of plant species to atrazine are due partly to environmental factors that alter atrazine absorption and translocation to stems and leaves. They assumed that if absorption and translocation rates are low, metabolic degradation of the herbicide may prevent accumulation of toxic amounts within the plants. Penner (1971) found increased atrazine phytotoxicity with increasing temperatures from 20 to 30°C. He suggested that a possible relationship exists between increased herbicide transport to the shoot at high temperature and increased phytotoxicity. At the high temperature, increased herbicide absorption, greater translocation from root to shoot, reduced capacity of the enzymes to inactivate the compound, or rate changes in the aforementioned factors might have resulted in accumulation of atrazine to phytotoxic amounts within the plants (Penner, 1971).

In a resistant species like maize (*Zea mays* L.) or grain sorghum (*Sorghum bicolor* L. Moench), atrazine is primarily metabolized to hydroxyatrazine before it reaches the chloroplasts (Norris & Fong, 1983). In susceptible species such as peas (*Pisum sativum* L.), beans (*Phaseolus vulgaris* L.) or oats (*Avena sativa* L.), it is primarily atrazine that reaches and accumulates in the chloroplasts (Shimabukuro & Swanson, 1969; Ezra & Stephenson, 1985).

Plant uptake of phytotoxic amounts of atrazine is shown by symptoms (chlorosis followed by necrosis) which follows the translocation pattern in sensitive plants (Ashton, De Villiers, Glen & Duke, 1977). Good (1961) and Couch & Davis (1966) found that triazines, substituted ureas, uracils and dipyridyls characteristically inhibit photosynthesis through inhibition of photosynthetic electron transport. Initially, Good (1961) and Tischer & Strotmann (1977) postulated that these herbicides exert their phytotoxicity primarily through inhibition of the excitation of electrons in the Hill-reaction of photosynthesis. The site at which herbicides inhibit the Hill-reaction was not identified, but was believed to be associated with the short wavelength absorbing pigment system located in chloroplasts (Moreland, 1965).

Recent findings by Fuerst & Norman (1991) suggest that atrazine binds to the D1 protein of the photosystem II reaction centre situated in thylakoid membranes in chloroplasts, thus blocking photosynthetic electron transport. The oxygen evolving process (Hill-reaction) of photosynthesis is closely associated with the photosystem II reaction centre where atrazine apparently exerts its influence. Treatment of sensitive plants with atrazine blocks the flow of electrons through photosystem II. According to Fuerst & Norman (1991), some weeds developed resistance to atrazine through mutations of serine 264 (an amino acid in the D1 protein) to glycine - a process that prevents atrazine from binding to the D1 protein, thus allowing unrestricted electron flow.

TRANSFORMATION PROCESSES

The above discussion of transfer processes involved in the determination of atrazine activity has dealt with some important components of the complex of factors which governs herbicide bioactivity and persistence in soil. Although degradation of herbicides in soil is only one component of this complex, it is generally considered to be the principal route for loss of most compounds from soil (Walker, 1987, 1989). Soils provide an ideal environment for many types of degradative processes. Soil is a dynamic and complex biological and chemical medium in which numerous variables interact to determine the degradation rate of a compound and, hence, its persistence. In this context, factors such as soil water content, temperature, soil texture, nutrient status, organic matter, pH and microbial activity are regarded as important variables. Degradation processes usually involve direct chemical transformation of the herbicide and the activities of soil microorganisms.

Aspects of soil properties

Organic matter content of soil could be of particular importance in determining the degradation rate and thus the persistence of atrazine. The dominant role of organic matter in the adsorption of atrazine was cited in the above discussion. Organic matter also regulates microbial activity of soil - with generally higher levels of biomass and respiration in more organic soils (Walker, 1989). The clay content of soil may also be important in determining atrazine persistence, because as pointed out earlier, it is an important predictor of atrazine availability in the soil solution. When working with natural soils, it can be difficult to separate the effects of clay and organic matter since

they are often correlated (Eagle, 1983a; Reinhardt & Nel, 1989). Clay content is an important component of soil texture, and soil texture can have a marked effect on other soil properties. Coarse-textured soils with low clay content tend to have less organic matter and lower microbial biomass than fine-textured soils (Walker, 1989). Soil texture will also influence pore size distribution in soil and consequently water relations and aeration characteristics.

Soil pH can have a pronounced effect on atrazine degradation rates. As pointed out earlier, pH exerts a direct effect when the stability of the chemical is pH dependent, or it has an indirect effect through changes in microbial populations, or through colloidal adsorption of the compound.

Aspects of temperature and water

In addition to the variability in herbicide degradation rates between soils, rates of loss may vary in a particular soil according to the water and temperature regimes encountered. In general, rates of herbicide loss increase with increases in temperature and soil water (Walker, 1989). Increased atrazine degradation rates with increasing temperature and soil water have been demonstrated in field experiments (Harris, Woolson & Hummer, 1969) and in laboratory incubation studies (Walker & Zimdahl, 1981). With many pesticides, Briggs (1983) and Walker & Allen (1984) demonstrated a 2 to 2.5 fold increase in half-life with a 10°C decrease in temperature, and a 1.5 to 2.5 fold increase in half-life if soil water is reduced by a factor of two. Weather conditions after herbicide application in the field should have a similar large effect on persistence. The weather, therefore, can have a marked influence on rates of atrazine

loss, and it is essential to be aware of this when evaluating field persistence data from different sites.

Chemical degradation

Chemical hydrolysis of atrazine to hydroxyatrazine is regarded as the main avenue of inactivation of the herbicide in soil (Armstrong, Chesters & Harris, 1967; Gamble & Khan, 1985). The atrazine molecule is stable under neutral pH conditions, but rapid chemical hydrolysis occurred under highly acid or alkaline conditions (Armstrong *et al.*, 1967). According to Weber (1970a), the Cl⁻ ion of the atrazine molecule is replaced with an OH⁻ ion through direct nucleophilic substitution under alkaline conditions. Under acid conditions, protonation of a ring or side chain N atom is followed by cleavage of the C-Cl bond by H_2O. Protonation of N would increase the electron deficiency of the C bonded to Cl, thus increasing the tendency for nucleophilic displacement of Cl by H_2O.

In studies with simazine (Walker *et al.*, 1983) and metribuzin (Allen & Walker, 1983), degradation rates decreased as adsorption on soil colloids increased, presumably due to decreased availability for degradation. Adsorption, however, does not always lead to protection from degradation, and examples of adsorption-catalyzed hydrolysis of some chlorotriazines, including atrazine, have been reported (Armstrong & Chesters, 1968; Hance, 1979). Armstrong *et al.* (1967) and Swain (1981) ascribed the major role of organic matter in the inactivation of atrazine in soil to its influence on the rate of atrazine hydrolysis. Organic matter evidently catalyzed hydrolysis by adsorption of

atrazine, accounting for the more rapid rate of hydrolysis in soils with a relatively high organic matter content compared to soil with low organic matter contents.

Microbiological degradation

As atrazine is chemically stable at neutral pH values (Armstrong *et al.*, 1967), it is likely to persist in many soils and chalky groundwater (Wood *et al.*, 1991) unless degraded by microorganisms. Kaufman & Kearney (1970) listed a large number of microorganisms that have the ability to degrade atrazine in pure culture, most of those reported being fungi. There are, however, reports of bacteria including *Arthrobacter* sp., *Bacillus* sp. and *Pseudomonas* sp. (Kaufman & Kearney, 1970; Cain & Head, 1991). Oxidative dealkylation appears to be the major mechanism by which microorganisms degrade atrazine, but degradation has also been observed under anaerobic conditions (Kaufman & Kearney, 1970).

SIGNIFICANCE OF PERSISTENCE

The above discussion has given an indication of how variations in some soil properties can influence rate of degradation through effects on adsorption, chemical transformation, or microbial breakdown. The end result is variability in degradation rate, and therefore, herbicide persistence that varies from soil to soil and from site to site. Residual soil-applied herbicides such as atrazine are an essential component of many crop production systems. The time that herbicides persist in the soil is of particular importance as this has already been shown to have serious implications for the safety

of sensitive following crops (Eagle, 1978; Caverley, 1983; Gottesbüren, Pestemer, Wang, Wischnewsky & Zhao, 1991).

From an agronomic viewpoint, the ideal herbicide should persist long enough to provide season-long weed control but not so long that its residues harm sensitive follow-up crops. Carry-over problems are likely to occur when soil and weather factors which favour reduced herbicide degradation prevail periodically or for a significant length of time subsequent to herbicide application; and when the particular follow-up crop is markedly sensitive to the specific herbicide residue. Excessive persistence tends to occur more frequently in some seasons than in others (Eagle, 1983b), reflecting the influence of climatic factors on rates of loss. Some soils are also more prone to carry-over problems than others. These problems are exacerbated by errors in initial application which lead to overdosing.

The absolute value for residual concentration will be determined by sampling depth; and phytotoxicity of residues will depend on soil type (Eagle, 1978; Williams, 1983), residue distribution in soil as modified by cultivation (Dragun & Helling, 1985) and leaching, and on weather conditions (Eagle, 1983b). High enough residual amounts to damage sensitive plants may be present in soil, but unavailability of the total amount due to adsorption may prevent plants being affected. However, should a particular set of environmental factors render the residues available for uptake by plants in high enough amounts, a phytotoxic effect will occur.